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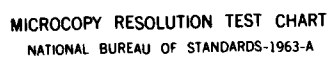
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Macrocycles Containing Tin.

^{119}Sn NMR Studies of Chloride Binding by Lewis Acidic Tin Compounds.
Multidentiate Effects, Macrocyclic Effects and Size Selectivity

by

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September 15, 1985

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Abstract: Three macrocyclic Lewis acidic hosts containing two symmetrically disposed dichlorostanna moieties (**1-3**, ring sizes 18, 22, 26 atoms, respectively) have been prepared as has an acyclic di-tin model (5,5,16,16-tetrachloro-5,16-distannadocosane, **4**). The complexation of **1-4** and dibutyltin dichloride (**5**) with chloride ion in acetonitrile was studied by ^{119}Sn NMR spectroscopy. Rapid exchange of chloride between tin atoms occurred at all ratios of chloride to host studied. An iterative computer program was used to provide estimates of the binding constants of **1**, **2**, **4** and **5** with chloride. Competition experiments were performed wherein two di-tin hosts competed for limited chloride ion, and the ^{119}Sn NMR spectra of the mixtures were analyzed to determine the relative amount of chloride bound by each host and hence the ratio of the binding constants for the two hosts. For the di-tin compounds there was good agreement between the relative binding constants found in the latter studies and the ratios of the absolute binding constants found in the former studies. The energies of binding were calculated. The di-tin hosts exhibited cooperative bidentate effects in binding chloride in comparison to **5** leading to an increase in binding energy over the amount predicted for a statistical correction in the number of sites. The cyclic hosts **1-3** bind chloride more strongly than acyclic model **4** (macrocyclic effect). Host **1** binds chloride somewhat more strongly than host **2** (size-selective effect).

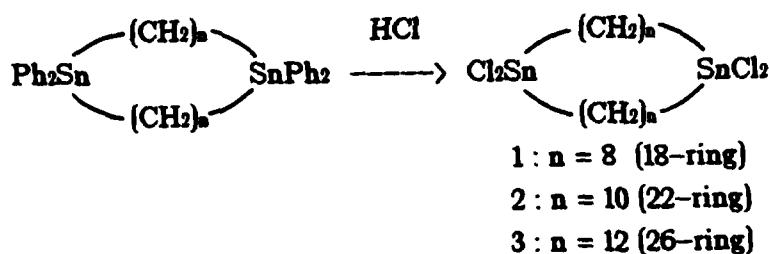
Over the past 15 years, host-guest chemistry has evolved from a novelty to a well developed area of study.¹ Extensive work has been reported in cation binding by basic hosts, but little has been reported on the binding of anions by charged hosts, and the binding of anions by neutral, Lewis acidic hosts is, with a few exceptions,² virtually unexplored. No cases of macrocyclic, Lewis acidic host binding of anion guests has been reported.

In this report we present the first studies of binding of an anion, chloride ion, by Lewis acidic macrocycles. ¹¹⁹Sn NMR spectroscopy was used to study complexation of chloride by three macrocyclic hosts containing two Lewis acidic tin atoms, a di-tin model and a mono-tin model. An iterative computer program was used to provide estimates for the binding constants of chloride by the hosts, and competition experiments were performed to measure the relative binding constants of two hosts for chloride ion.

Preparation of Hosts

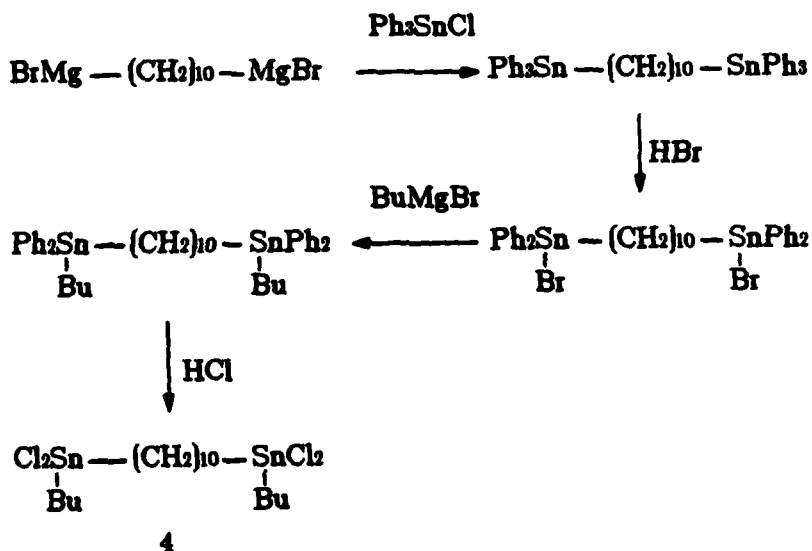
We have reported the syntheses of macrocycles containing two or four tin atoms.³ These macrocycles contained diphenylstanna moieties linked by polymethylene chains and, as such, were poor Lewis acids. However, conversion of the tin moieties of these compounds to dichlorostanna groups gave Lewis acidic species. Cleavage of the phenyl groups on tin was accomplished with high selectivity by treatment of the diphenylstanna compounds with excess anhydrous HCl in CH₂Cl₂ to give dichlorostanna macrocycles **1-3** (Scheme 1). The compounds are sharp melting solids which show only one tin resonance in their ¹¹⁹Sn NMR spectra.

Scheme 1



In preliminary studies, it appeared that 22-membered ring macrocycle **2** bound chloride more strongly than did **1** or **3**. Thus, for comparison, acyclic model compound **4** was prepared by the sequence shown in Scheme 2. Dibutyltin dichloride (**5**) was used as a model for a mono-tin containing species.

Scheme 2



¹¹⁹Sn NMR Spectroscopy Studies of Chloride Binding by Acidic Hosts

Dialkyltin dichlorides bind chloride ion strongly, and it is possible to isolate a complex of **5** with tetraethylammonium chloride.⁴ However, in the polar aprotic solvent acetonitrile, this complex is soluble. Thus, we could study the effect on the ¹¹⁹Sn NMR spectra of the Lewis acidic tin compounds **1-5**

in acetonitrile as chloride was added. Compounds **1-5** in acetonitrile display chemical shifts in the range of 50-60 ppm relative to tetramethyltin which is a typical range for tetrahedral tin atoms.⁵ Upon addition of increments of tetraethylammonium chloride to the solutions, we observed only a single resonance which gradually shifted upfield as the ratio of chloride to tin was increased. The single signal indicated rapid exchange of chloride ion and that a weighted average signal of the various species present was observed. As the Cl⁻/Sn ratio was increased to greater than one, the chemical shifts reached a plateau value at -128 to -131 ppm which is a typical range for pentacoordinate tin atoms.⁵

The ¹¹⁹Sn NMR spectra of hosts **1-4** were measured as successive increments of 0.05 mol-% of tetraethylammonium chloride were added. The chemical shift of the host was a smooth function of the Cl⁻/Sn ratio which was increased from 0.0 to 1.2. Tables 1-4 list the experimental data for the ¹¹⁹Sn NMR spectra of species **1-4** in the presence of varying amounts of tetraethylammonium chloride. For dibutyltin dichloride we also observed a smooth chemical shift change as incremental amounts of chloride were added up to one 1.2 molar equivalents (Table 5).

Table 1. Observed ^{119}Sn NMR chemical shifts for mixtures of Host 1 and tetraethylammonium chloride in acetonitrile.

[Host 1], M	$[\text{Cl}^-]$, M	^{119}Sn NMR chem shift
0.1250	0.0000	56.7
0.1190	0.0119	46.5
0.1136	0.0227	35.8
0.1042	0.0417	15.8
0.1000	0.0500	5.6
0.0962	0.0577	- 4.0
0.0926	0.0648	- 13.4
0.0893	0.0714	- 22.5
0.0862	0.0776	- 32.2
0.0833	0.0833	- 41.4
0.1250	0.1250	- 37.2
0.1190	0.1310	- 46.3
0.1136	0.1364	- 55.2
0.1087	0.1413	- 63.8
0.1042	0.1458	- 72.5
0.1000	0.1500	- 80.8
0.0962	0.1538	- 89.1
0.0926	0.1574	- 97.2
0.0893	0.1607	-105.1
0.0862	0.1638	-112.5
0.0833	0.1667	-119.3
0.1250	0.2500	-120.0
0.1190	0.2500	-125.3
0.1136	0.2500	-129.1
0.1087	0.2500	-129.0
0.1042	0.2500	-131.0
0.1000	0.2500	-131.3
0.0962	0.2500	-131.4

Table 2. Observed ^{119}Sn NMR chemical shifts for mixtures of Host **2** and tetraethylammonium chloride in acetonitrile.

[Host 2], M	$[\text{Cl}^-]$, M	^{119}Sn chem shift
0.1250	0.0000	57.3
0.1190	0.0119	46.3
0.1136	0.0227	35.9
0.1087	0.0326	24.7
0.1042	0.0417	16.6
0.1000	0.0500	4.4
0.0962	0.0577	- 5.2
0.0926	0.0648	- 14.8
0.0893	0.0714	- 24.4
0.0833	0.0833	- 40.1
0.1250	0.1250	- 39.1
0.1190	0.1310	- 48.0
0.1136	0.1364	- 56.6
0.1087	0.1413	- 65.1
0.1042	0.1458	- 74.2
0.1000	0.1500	- 82.1
0.0962	0.1538	- 90.4
0.0926	0.1574	- 98.0
0.0893	0.1607	-105.4
0.0862	0.1638	-112.8
0.0833	0.1667	-119.0
0.0806	0.1694	-124.2
0.0781	0.1719	-127.3
0.0758	0.1742	-128.9
0.0735	0.1765	-129.4

Table 3. Observed ^{119}Sn NMR chemical shifts for mixtures of Host **3** and tetraethylammonium chloride in acetonitrile.

[Host 3], M	$[\text{Cl}^-]$, M	^{119}Sn chem shift
0.1250	0.0000	55.9
0.1190	0.0119	47.0
0.1087	0.0326	31.0
0.1042	0.0417	22.6
0.1000	0.0500	13.8
0.0962	0.0577	5.0
0.0926	0.0648	- 4.5
0.0893	0.0714	- 13.8
0.0862	0.0776	- 22.9
0.0833	0.0833	- 32.1
0.1250	0.1250	- 31.7
0.1190	0.1310	- 39.0
0.1136	0.1364	- 48.0
0.1087	0.1413	- 55.8
0.1042	0.1458	- 63.9
0.1000	0.1500	- 71.7
0.0640	0.1280	-117.7

Table 4. Observed ^{119}Sn NMR chemical shifts for mixtures of host **4** and tetraethylammonium chloride in acetonitrile.

[Host 4], M	$[\text{Cl}^-]$, M	^{119}Sn chem shift
0.1250	0.0000	47.5
0.1190	0.0119	37.9
0.0595	0.0119	26.1
0.0581	0.0174	16.9
0.1000	0.0500	0.4
0.0962	0.0577	- 8.4
0.0926	0.0648	- 17.5
0.0893	0.0714	- 25.7
0.0862	0.0776	- 34.6
0.0833	0.0833	- 41.8
0.0806	0.0887	- 52.0
0.0781	0.0938	- 56.3
0.0758	0.0985	- 65.7
0.0735	0.1029	- 75.8
0.0714	0.1071	- 82.5
0.0694	0.1111	- 90.4
0.0676	0.1149	- 97.2
0.0658	0.1184	-104.0
0.0641	0.1218	-110.5
0.0625	0.1250	-116.0
0.0610	0.1280	-120.3
0.0595	0.1310	-123.1
0.0581	0.1337	-124.0
0.5682	1.3636	-125.0

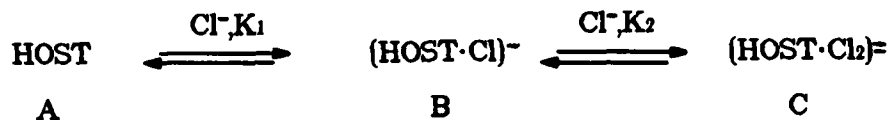
Table 5. Observed ^{119}Sn NMR Chemical Shifts for mixtures of dibutyltin dichloride (5) and tetraethylammonium chloride in acetonitrile.

$[\text{Bu}_2\text{SnCl}_2]$, M	$[\text{Cl}^-]$, M	^{119}Sn chem shift
0.50	0.00	48.7
0.50	0.05	31.0
0.50	0.10	9.8
0.50	0.15	- 7.3
0.50	0.20	- 22.5
0.50	0.25	- 40.5
0.50	0.30	- 54.3
0.50	0.35	- 71.1
0.50	0.40	- 84.1
0.50	0.45	- 94.9
0.50	0.50	-108.3
0.50	0.55	-118.2
0.50	0.60	-119.1
0.50	0.65	-121.7

Qualitative Evaluation of Chloride Binding

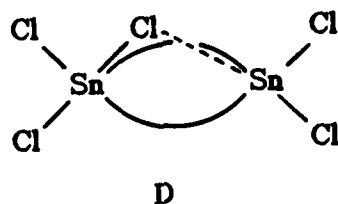
The measured chemical shifts in Tables 1-5 are weighted averages of all of the tin species in solution. We made the simplifying assumption that for the host compounds 1-4 the predominant species in solution were uncomplexed species (A), the monochloride complex (B) and the dichloride complex (C) (Scheme 3). The ^{119}Sn NMR chemical shift of A is measured in the absence of added chloride salt, and the ^{119}Sn NMR chemical shift of C may be estimated as the chemical shift observed in the presence of excess chloride salt. With these assumptions one can make two qualitative observations concerning chloride complexation.

Scheme 3



(1) The binding constants for chloride are large. These mixtures were relatively dilute, and within a given set of measurements the host concentration varied by a factor of two. Nevertheless (a) the measured chemical shift differences (relative to zero chloride) of the host species in the presence of one equivalent of chloride ion per mole of host species were greater than one-half of the chemical shift differences seen with excess chloride ion; (b) the chemical shift limiting values were reached at slightly greater than two equivalents of chloride ion per mole of host; (c) smooth changes in chemical shifts were observed as host concentrations were reduced overall by the addition of chloride solution; and (d) when host and chloride concentrations were both doubled (providing potentially a large change in complex concentrations if the complexation constants were small), the chemical shifts were unchanged (<1 ppm difference). We conclude that the association constants must be large for both K_1 and K_2 in Scheme 3.

(2) Cooperative effects apparently are present in 1:1 complexes of chloride and hosts. For hosts **1**, **2** and **4** where complete data sets were measured, the chemical shifts at Cl^- to host ratios of 1:1 are greater than one-half of the total chemical shift difference seen between chloride to host ratios of 0:1 to 2:1. In fact, the chemical shifts at 1:1 ratios appear to be greater than one-half of the total chemical shift difference between zero and excess chloride ion. Within the constraints of the assumption that A, B and C are the predominant species in solution, and given the smooth chemical shift changes observed from zero to excess chloride, it is required that the 1:1 complex (B) reached its maximum concentration in the vicinity of a 1:1 molar ratio of chloride to host. Either (a) the binding constant K_1 in Scheme 3 is much larger than K_2 and at chloride to host molar ratios of 1:1 essentially only B is present; or (b) in the complex B the bound chloride ion interacts with the remote tin atom (structure D); or (c) there is a combination of these two cooperative effects.



By our assumption that A, B and C are the predominant species in solution, we have excluded the possibility that intermolecular bridging of two tin compounds by chloride leads to the observed chemical shift values at 1:1 molar ratios of chloride to host. Such intermolecular effects apparently are observed in the study with **5** where the chemical shift at a 0.5:1 ratio of chloride to **5** is about 10 ppm upfield of the average value of a 0:1 and a 1:1 mixture of chloride and **5**. However the data for chloride binding by **5** was obtained with solutions which were five times the concentration of the solu-

tions used in the studies of 1-4, and the chemical shift value at the 0.5:1 (Cl^- to 5) point was exactly the average of the values measured in the absence of chloride and in the presence of excess chloride. We conclude that intermolecular bridging of hosts by chloride is of little consequence for the di-tin hosts.

Quantitative Evaluation of Chloride Binding

In principle, it should be possible to extract from the data in Tables 1-4 the binding constants K_1 and K_2 in Scheme 3. With the assumption that species A, B and C are the predominant species in solution, we wrote an iterative computer program based on a published model for generalized curve fitting⁶ which was used to calculate the association constants. The program was flexible enough to permit several models for binding, and in its most general form it could solve for the five variables δ_A , δ_B , δ_C , K_1 and K_2 to find the best fit for the NMR data where the observed chemical shift is a weighted average of the shifts for A, B and C. Any or all of the variables could be either fixed or varied by predetermined initial amounts in the fitting procedure.

Since we could estimate the chemical shift of A (δ_A) and that of C (δ_C) with reasonable certainty, we hoped that the program would converge on consistent values of δ_B and K_1 and K_2 . However, the program failed to converge to a unique minimum solution when δ_B , K_1 and K_2 were varied. Essentially, there were two or more minima found for the complexations of 1, 2 and 4 with chloride, and these minima were a function of the initial value assigned to δ_B .

However, it was possible to solve the data in Tables 1, 2 and 4 in an acceptable manner. When we assigned an initial value of $\delta_B = -48$ ppm and then performed successive iterations altering first the three chemical shift values and then the two association constants, we consistently found solutions for the

five variables which gave the smallest errors relative to the observed data (chi-square test). With the caveat that these values are constrained to the region surrounding $\delta_B = -48$ ppm, the results are given in Table 6. It was satisfying that when permitted to vary, the values for the chemical shifts of species A and C were found to be quite close to the experimental values. The data in Table 3 was not successfully treated by our program which consistently minimized the solution to give an unreasonable chemical shift for B.

Table 6. Optimized solutions for the chemical shifts for δ_A , δ_B , δ_C and binding constants K_1 and K_2 found by generalized curve fitting.^a

Host	δ_A (ppm)	δ_B (ppm)	δ_C (ppm)	K_1 (M ⁻¹)	K_2 (M ⁻¹)
1	56.4	-48.0	-127.2	814	863
2	55.7	-48.2	-129.3	684	556
4	46.0	-48.2	-130.8	427	527
5 ^b	46.6		-130.2	110	

^a Model in Scheme 3; initial values: δ_A = observed value in Table 1, 2 or 4; δ_B = -48 ppm, δ_C = -132 ppm, $K_1 = K_2 = 500$ M⁻¹. ^b Model in Scheme 4; initial values: $\delta_A = 48.7$ ppm, $\delta_C = -128$ ppm. See text for details.

The binding constant for the acyclic, mono-tin model 5 was determined by the iterative program where we assumed that only the species in Scheme 4 were present. In this case the value of the chemical shift of C and that of the binding constant were closely linked. There was a broad flat region in the set of solutions around the best fit. The best solution for the data in Table 5 was $K_1 = 60$ M⁻¹ and $\delta_C = -137.7$ ppm, but we believe this value for the chemical

shift of C is unreasonable. When we constrained the solutions such that the value for δ_C could not be less negative than ca. -130 ppm, we found the optimized solution given in Table 6. This solution was only slightly poorer than the best fit; the chi-square value was only 13% higher than the value of chi-square for the best fit.

Scheme 4



From the calculated values for the association constants, it appears to be sound to conclude that the di-tin hosts **1**, **2** and **4** show a bidentate effect in comparison to **5**. Further, the results in Table 6 suggest that the 18-membered and 22-membered ring macrocycles (**1** and **2**) exhibit a "macrocyclic effect" in that they bind chloride more strongly than the acyclic di-tin host **4**. It also appears from this data that there may be a small "size selective effect" in that the 18-membered ring host binds chloride somewhat more effectively than the 22-membered ring host.

The results in Table 6 must be viewed with some caution. Since K_1 and K_2 were both large and similar in value, plots of chemical shift versus chloride concentration were only slightly curved. This is exactly the type of data which the multiparameter program might fit poorly. The results of our competitive binding studies (*vide infra*), however, support the conclusions obtained from the results in Table 6.

Direct Determination of Relative Binding Efficiencies

Competitive binding studies were performed by mixing two Lewis acidic di-tin hosts in acetonitrile and adding a deficiency of tetraethylammonium chloride to the solution. When the ^{119}Sn NMR spectra of these mixtures were recorded, we observed one peak for each host. By using a 2:1 mixture of host X and host Y, it was easy to assign the ^{119}Sn NMR peaks. The measured chemical shifts for each host were compared to the plots of chemical shift versus chloride concentration from the data in Tables 1-4. This permitted us to assign the number of moles of chloride bound by each host and to calculate the complexed and free mole fractions of each host.

At low chloride to host ratios, we may assume that little of the dichloride complex (C) is present, and the amounts of chloride bound by each host reflect the K_1 of the host. The K_1 's for hosts X and Y can be compared from the chemical shift data as shown in the simple derivation below. It is noteworthy that the absolute amounts of a host used are not important since only the ratio of complexed to free host are needed in Equation 3. It also should be noted that this approach is an oversimplification and applies only at low chloride to host ratios. As the chloride to host ratio is raised, the second complexation constants will become important and the percentage of chloride bound by host X and host Y should change.

$$K_{1X} = [\text{X}\cdot\text{Cl}^-] / [\text{X}] [\text{Cl}^-] , \quad K_{1Y} = [\text{Y}\cdot\text{Cl}^-] / [\text{Y}] [\text{Cl}^-] \quad (1)$$

$$[\text{Cl}^-] = [\text{X}\cdot\text{Cl}^-] / [\text{X}] K_{1X} = [\text{Y}\cdot\text{Cl}^-] / [\text{Y}] K_{1Y} \quad (2)$$

$$K_{1X} / K_{1Y} = [\text{X}\cdot\text{Cl}^-] / [\text{X}] * [\text{Y}] / [\text{Y}\cdot\text{Cl}^-] \quad (3)$$

Table 7 lists the results of the competitive binding studies with di-tin hosts 1-4. The chloride to host ratio was maintained below 1:1, but one can see that as this ratio increased the relative binding constants of two hosts

were altered as was expected. We also have listed the calculated value of K_{1X}/K_{1Y} using the constants in Table 6. Unfortunately, mono-tin model 5 could not be compared to the di-tin hosts directly; when these studies were attempted, we observed only broad signals in the ^{119}Sn NMR spectra.

Table 7. Results of Competitive Binding Experiments.^a

Host X	Host Y	$\text{Cl}^-(\text{mol-\%})^b$	δ_X	δ_Y	K_{1X}/K_{1Y}	$K_{1X}/K_{1Y}(\text{calcd})^c$
1	4	0.05	40.5	38.7	1.81	1.91
		0.15	17.6	22.8	1.52	
		0.40	-31.2	-20.3	1.39	
		0.80	-97.1	-90.1	1.42	
2	4	0.30	1.2	4.9	1.34	1.61
		0.40	-20.7	-14.5	1.24	
		0.60	-61.4	-53.1	1.36	
3	4	0.20	17.2	18.0	1.41	
		0.40	-20.4	-15.2	1.41	
		0.80	-90.3	-82.9	1.25	
1	2	0.30	- 2.1	4.0	1.23	1.18 (1.1) ^d
		0.60	-63.2	-62.8	1.14	

^a See text for description of the experiment and rationale. ^b Mol-% of chloride relative to the sum of the moles of hosts. ^c Calculated from the association constants in Table 6. ^d Calculated from the ratios of experimental relative association constants of 1 to 4 and 2 to 4.

Even qualitative observations of the ^{119}Sn NMR spectra of the competition experiments with the cyclic hosts **1-3** versus acyclic host **4** clearly showed that the cycles bound chloride more strongly than **4**. The signal from **4** in the absence of chloride was upfield of the signals from **1-3** in the absence of chloride, yet at chloride mol-% values of 0.15 or greater, the signal from the cyclic host had moved upfield of that from **4**. The results in Table 7 show the same trends we had seen in the absolute values of the association constants listed in Table 6 for hosts **1**, **2** and **4**. The macrocyclic effects and a small size selective effect are seen in binding chloride.

The favorable comparisons of K_{1X}/K_{1Y} determined in the competition experiments against those calculated from the values in Table 6 are important because they indicate that the assumptions and restrictions imposed in the calculations in Table 6 were reasonable, and they suggest that the absolute values for K_1 found by our method are reasonably accurate.

Energies of Binding

The free energies ($-\Delta G$) of the first binding constant for binding chloride in acetonitrile by hosts **1**, **2**, **4** and **5** may be calculated from the binding constants in Table 6, and the differences in free energies ($-\Delta\Delta G$) of binding between two hosts can be calculated from the data in Tables 6 and 7. Table 8 contains the results.

It should first be noted that we start with a relatively strong binding in the model compound **5** of 2.82 kcal/mol. A statistical effect of adding a second binding site which did not have any cooperative effect would raise the binding energy to 3.24 kcal/mol. We clearly have cooperative binding effects in the di-tin hosts since the binding energies are 3.63 to 4.02 kcal/mol for **1**, **2** and **4**. Thus, the cooperative, bidentate effect raises the binding energy of acycle **4** in comparison to **5** by about 0.4 kcal/mol more than expected from the statis-

tical effect. These are important values when one considers the potential binding energies of ligands containing several Lewis acidic sites. The statistical effect of increasing binding sites becomes increasingly less important, i.e. increasing from one to six sites would only give a 1.1 kcal/mol increase in binding strength. However, the cooperative, interactive effects of several binding sites are not expected to decrease in magnitude as the binding sites' number increases, and, indeed, may increase in magnitude.

Macrocyclic effects are also clearly present in hosts **1-3** in comparison to host **4**. The macrocycle effect raises the binding energies by 0.1 to 0.4 kcal/mol over that of the di-tin acycle. When one considers that only two binding sites are present in our hosts and realizes that the conformational constraints of the macrocycle should only provide a minimum increase in organization of the cyclic host's binding sites relative to those in acycle **4**, these results are quite encouraging. Again, we conclude that in multi-site hosts we should expect to see yet larger effects.

With the flexible hosts we studied, one would expect to find virtually no size selective behavior in chloride binding. However, a small but real size selective effect is seen in the comparison of the chloride binding ability of the 18-membered ring host **1** to the 22-membered ring host **2**. Rigid hosts are expected to display dramatic selectivity effects.

With these values we might speculate on the behavior of a four site Lewis acidic host. The statistical effect of four sites will increase binding strength by ca. 0.8 kcal/mol ($-RT \ln 4$). The polydentate effect should increase binding by at least 1.2 kcal/mol and the macrocycle effect should provide an additional increase in binding strength of 0.4 kcal/mol for an optimum ring size. The minimum predicted binding energy is 5.2 kcal/mol which would correspond to a binding constant of ca. 6000 M^{-1} . When we attempted to study

chloride binding by a macrocycle containing four Lewis acidic tin atoms, insoluble precipitates formed; thus, a different experimental method of attack is needed.

Table 8. Host-chloride binding energies in acetonitrile.^a

Binding energies:	Host	$-\Delta G$, kcal/mol	
	1	4.02	
	2	3.92	
	4	3.63	
	5	2.82	
Bidentate effect:	Hosts compared	$-\Delta\Delta G$, kcal/mol	
	1 vs 5	1.20	
	2 vs 5	1.10	
	4 vs 5	0.81	
	statistical	0.41	
Macrocyclic effect:	Hosts compared	$-\Delta\Delta G$, kcal/mol	
		Table 6	Table 7
	1 vs 4	0.38	0.19-0.35
	2 vs 4	0.28	0.13-0.18
	3 vs 4		0.13-0.20
Size selectivity:	1 vs 2	0.10	0.08-0.12

^a At 30 °C, calculated for the first binding constants for the di-tin hosts.

Conclusion

The Lewis acidic hosts exhibit the same trends in binding the chloride anion as basic hosts display in binding cations. When two acidic sites are incorporated into hosts 1-4, the binding constants are substantially greater than that of the mono-tin model dibutyltin dichloride (5). The cyclic hosts 1-3 bind chloride more strongly than the acyclic host 4, a macrocyclic effect. Within the series of macrocycles, the 18-membered ring host (1) binds chloride somewhat more strongly than the larger ring hosts, this effect is most likely a size-selective effect.

The magnitude of the effects we have found in the di-tin hosts 1-4 are modest in comparison to those known for basic hosts, but that derives from the fact that our hosts have only two binding sites and was not unexpected. Since the values for binding energies we have found for bidentate and macrocyclic effects are greater than the statistical effects, we can predict with confidence that hosts with four or six binding sites will show large changes in binding energies. Size selectivity is low for our hosts because they contain long polymethylene chains which are quite flexible, and thus they lack the rigidity which leads to exceptionally high selectivity in binding.

It is expected that large increases in anion binding strengths and large differences in selectivity will result from rigid macrocyclic hosts containing several Lewis acidic sites. In terms of percentages of substrate bound by hosts, it is also important to note that greater differences in anion percentage binding will result from hosts containing poorer Lewis acidic moieties than those in the compounds we studied, i.e. hosts containing less electronegative groups on tin.

Experimental Section

Preparation of hosts 1-3. We have reported the preparation of the

1,1,n,n-tetraphenyl-1,n-distannacycloalkanes.³ Gaseous HCl was bubbled through methylene chloride at -78 °C to give a saturated solution. The solution was allowed to warm to room temperature, and an aliquot was removed, added to water and titrated with a standardized base solution to determine the concentration of acid. The CH₂Cl₂ solution of HCl was added to a solution of the tetraphenyldistanna macrocycle in CH₂Cl₂ at -78 °C such that ca. five molar equivalents of acid were added in all. After 6-8 h, the reaction mixture was allowed to warm to room temperature. The reaction mixture was concentrated under reduced pressure to give a crude solid product. Recrystallization from CH₂Cl₂--hexane (ca. 1:3, v:v) gave white, crystalline products which were characterized by ¹H and ¹¹⁹Sn NMR spectroscopy. There was no indication of bond cleavage between the tin atoms and the methylene units in the macrocycles. Host **1** had mp 84-86 °C; host **2** had mp 90-92 °C; host **3** had mp 97-99 °C; host **4** had mp 85-87 °C.

¹¹⁹Sn NMR Studies Spectra were recorded at 30 MHz on a Varian FT-80 at 30 °C using a standard pulse sequence which provided ¹H decoupling but eliminated n.O.e effects. All chemical shifts are reported relative to internal tetramethyltin. A solution of host in 5 mL of acetonitrile containing ca. 0.2 mL of benzene-d₆ (for a lock signal) and ca. 0.1 mL of tetramethyltin was prepared, standard solutions of tetraethylammonium chloride were added, and spectra were recorded. Generally, a single sharp signal was observed for the host, but a few of the spectra showed broad signals and these spectra were not used. The results are given in Tables 1-5.

The competition experiments were performed by mixing two hosts (ca. 0.3 mmol of one host and ca. 0.6 mmol of the second) in 5 mL of acetonitrile with benzene-d₆ and tetramethyltin. A weighed amount of tetraethylammonium chloride was added, and the spectrum was recorded. The results are given in Table 7.

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